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ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT

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Office of Naval Research
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Project Scientist
Captain Steve Snyder

Abstract
Purified chitin samples have been compared to the controls with optical, stereo and SEM microscopy to identify regional coverage. Evidence from new tests show that sieving is required to produce a more evenly dispersed and invariable chitin grain size. These tests indicate that, after sieving, there is no discernible difference between the purified chitin dispersion versus the unpurified material dispersion in the paint/thinner mixture. Polished and dipped samples have been produced and evaluated for anti-icing qualities. A series of icebox, icephobic tests have been completed showing the icing effects of particle size, dispersal percentages, polishing, and dipping. A marine bath system was developed to continue icephobic testing under oceanic conditions. Initial fungi tests have been structured to test sample repulsion to fungal environments and analytical evaluations and ASTM testing have begun. Research and engineering of new preparation and evaluation systems have been instituted. Analytical methods are being studied to attempt stable chemical alterations of the chitin before mixing with the paint. Also, new chitin/chitosan materials and paint representatives have been acquired to further refine the current preblend paint suspension system.

Identifiers/Open-Ended Terms
Chitin
Chitosan
Icephobic Paint
Antifouling Paint
Enzymatic Degradation of Paint

Availability
Defense Technical Information Center
Bldg. 5, Cameron Station
Alexandria, Virginia 22314

Security Class
Unclassified
Unlimited

TABLE OF CONTENTS

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FORWARD

This Technical Report covers work performed on Contract N00014-90-C-0062, entitled " ANTI-ICING CHITIN COATING SYSTEM DEVELOPMENT", technically through May 1, 1990 through June 30, 1990. This program was sponsored by the Office of Naval Research, 800 North Quincy Street, BCT #1, Arlington, Virginia 22217-5000. The Project Scientist was Captain Steve Snyder.

Mrs. Gail Bowers-Irons was both the Project Manager and Principal Investigator. Both Mr. Craig T. Miller and Ms. Amy Lai were responsible for this quarter's icephobic, antifungal and enzymatic testing.

SUMMARY

Technical Objective:

The objectives of this project are to develop a standard icephobic chitin/chitosan paint system that can be easily and inexpensively produced and employed; to determine if the chitin/chitosan paint mix is effectively antifouling and to determine if the chitin/chitosan paint mix can be efficiently biostripped via chitinase reaction.

Work Statement:

The project will be divided into five tasks. Task I will focus on the development of homogenous chitin or chitosan suspensions. Once the chitin and chitosan addition techniques are optimized, Task II work will determine the chitin/chitosan-paint suspensions standard ASTM test characteristics. Tasks III, IV and V will then center on the icephobic, antifouling and biostripping investigations.

Approach:

The work in this project will first focus on the production of homogenous chitin or chitosan suspensions. These suspensions would then be added to Mil Spec polyurethane or epoxy paints in order to provide icephobic, antifouling and biodegradable coatings. ASTM coating tests will then be run to determine stability and consistency.

Second Report Work To Date:

Purified chitin samples have been compared to the controls with optical, stereo and SEM microscopy to identify regional coverage. Dispersal percentages in the 10-15% range are the optimum for icephobic qualities. Mesh sizes of -200 and smaller are the optimum for our applications. A marine bath system was developed to continue icephobic testing under oceanic conditions but more work needs to be done for more qualitative information on icephobic traits. The Protan Sea Cure 350 purified chitin looks best in both preblend mixing and in the icephobic testing. Preliminary information will soon be analyzed on the fungi testing. Analytical methods are being studied to attempt stable chemical alterations of the chitin before mixing with the paint. Also, operations have begun on ASTM testing and evaluation of the materials already produced.

INTRODUCTION

The most recent International Conference on Chitin and Chitosan, held in Trondheim, Norway, surveyed many new chitin and chitosan commercial applications (Skjak). The conference leaders found that the commercialization of chitin and chitosan-containing products has stimulated academic and industrial research and development and has led to a search for new and recovered sources of materials. Therefore, commercial suppliers and users are formulating specifications and standards to ensure that their products will meet the criteria of *in vivo* use.

In TRA's work, purified chitin samples have now been compared to the controls with optical, stereo and SEM microscopy to identify regional coverage. First tests indicate that, after sieving, there is no discernible coating difference between the purified chitin dispersion versus the unpurified material dispersion in the paint/thinner mixture but sieving is required to produce a more evenly dispersed and invariable chitin grain size. Examination of these samples reveal a very smooth, fine grained, and well dispersed layer of chitin throughout the painted surface with both pure and unpure, sieved materials.

To evaluate the anti-icing properties of both purified and unpurified materials, TRA researchers have polished and dipped samples; run a series of icebox, icephobic tests to show the icing effects of particle size, dispersal percentages, polishing, and dipping and developed a marine bath system to continue icephobic testing under oceanic conditions.

They have also structured initial fungi tests to test sample repulsion to fungal environments and begun analytical evaluations and ASTM testing. Research and engineering of new preparation and evaluation systems have been instituted and analytical studies are underway to attempt stable chemical alterations of the chitin before mixing with the paint. Also, new chitin/chitosan materials and paint representatives have been acquired to further refine the current preblend paint suspension system. These new tests, and others, will be continued throughout the project to obtain the most effective and productive chitin or chitosan/paint mix.

PROCEDURES

Materials

In addition to the materials used in report ONRC1. (4/30/90) the following chitin/chitosans have been tested:

Sigma C-8908-Lot 59F7265-Chitin-Purified Shrimp Shell Powder

Sigma C-3641-Lot 107F-7115-Chitin-Purified Crab Shell Powder

CTC Organics-Lot 00430A-Chitin

CTC Organics-Lot 00430B-Chitosan

Protan Sea Cure 350. Lot CSN478 Chitin.

Temperature of reaction were ambient and additional approaches have now been tested to prepare stable and uniform suspensions or dispersions of chitin and chitosan in the paint.

SEM Inspection

SEM inspection was used (on previously described test samples) to indicate where the chitin/chitosans were located; however, it was difficult to tell if the chitins were forming aggregates. Noticeable differences could not be seen between different brands and types of chitin. The control samples showed that the painted surface alone appeared extremely rough even at low magnifications. A stereo microscope was later used (with much more success) to show the percent dispersion of the aggregates over the total painted surface. The following samples painted with different chitin/chitosan additives were scrutinized under the scanning electron microscope (SEM):

Sample	Photo No.	Magnification
S7-BT-100-5	1550	200X
S7-BT-100-5	1551	1000X
S7-BT-200-4	1552	200X
S7-BT-200-4	1553	480X
S7-BT-200-5	1554	200X
S7-BT-200-5	1555	320X
P2-BT-200-4	1556	200X
P2-BT-200-5	1557	200X
CONTROL-BT	1558	200X
CONTROL-BT	1559	1000X
S6-BT-200-1	1560	200X
S2-BT-200-2.86	1561	200X
P2-BT-100-5	1562	200X

S7=Sigma C-3387, P2=Pfaltz & Bauer C07632, S6=Sigma C-4666, BT=Paint plus Thinner as indicated in First Report.

Purified Chitin Samples

Dispersals of 3, 5, 10, and 15% were mixed with Rust-Oleum gray paint (40ml) and thinner (5ml). Mesh size was reported by Sigma to be <-100 mesh, so no additional sieving was performed. The following samples were produced with purified chitin (Sigma C-3641-Lot 107F-7115-Purified Chitin from Crab Shells).

<u>Samples</u>
S1-GT-3
S1-GT-5
S1-GT-10
S1-GT-15

Evidence from these test samples showed that sieving was required to produce a more evenly dispersed chitin grain size. The chitin particles appeared (stereo microscope) to cover the painted surface evenly in each different dispersal percentage and inspection also revealed that larger grains were not agglomerated as they first appeared. The next tests used mesh sizes of -140 to -200 to sift the purified chitin for the following samples:

<u>Samples</u>
S1-GT-140-3
S1-GT-140-5
S1-GT-140-10
S1-GT-200-3
S1-GT-200-5
S1-GT-200-10

Examination of these samples revealed a very smooth, fine grained, and well dispersed layer of chitin throughout the painted surface. Sieving is required for invariable particle size distributions. After sieving, there was no discernible difference between the purified chitin dispersion versus the unpurified material dispersion in the paint/thinner mixture.

Sample Production Summary

Table "CHITIN.XLS" refers to samples produced to date using the methods explained in <u>ONRC1</u>, pg. 4, 4-30-90. The following observations were made during the manufacturing processes:

1. Chitin/chitosan additives are visible on the dried paint surface regardless of particle size.
2. Dispersals $\geq$ 10% are difficult to apply evenly over the entire sample surface.
3. 20% dispersals saturate the surface with chitin/chitosan.
4. The homogenizer effectively disperses aggregates more uniformly than hand mixing.
5. Stereo microscopy shows that 1 and 2% dispersals do not effectively cover the sample surface.
6. Samples with particle sizes $\geq$ 80 mesh appear too coarse for our purposes.

CHITIN.XLS

	A	B	C	D	E	F
1	SAMPLE	TYPE	PAINT MIX	MESH	DISP. %	COMMENTS
2	S7-B-45-1	SIGMA C'IN C-3387	40mL B only	'-45+80	1	aggregates too large
3	S7-BTU-45-1	SIGMA C'IN C-3387	B+5mL TH+10m US	'-45+80	1	aggregates too large
4	S7-BTU-45-2	SIGMA C'IN C-3387	B+5mL TH+10m US	'-45+80	2	aggregates too large
5	S7-BT-80-1	SIGMA C'IN C-3387	40mL B+5mL TH	'-80+100	1	aggregates too large
6	S7-BT-80-2	SIGMA C'IN C-3387	40mL B+5mL TH	'-80+100	2	aggregates too large
7	S7-BT-80-3	SIGMA C'IN C-3387	40mL B+5mL TH	'-80+100	3	aggregates too large
8	SO-BT-?-.91	METHYLGLYCOL C'SAN	40mL B+5mL TH	UNKNOWN	0.91	aggregates too large
9	P2-BEA-100-1	PFALTZ & BAUER C'IN	B+5mL ethyl acetate	'-100+200	1	did not reduce agg. size
10	CONTROL-BT	NONE	40mL B+5mL TH	***	***	paint +thinner only
11	S7-BT-100-1	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	1	aggregates too large
12	S7-BT-100-2	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	2	aggregates too large
13	S7-BT-100-3	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	3	aggregates too large
14	S7-BT-100-4	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	4	aggregates too large
15	S7-BT-100-5	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	5	aggregates too large
16	P2-BT-100-1	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	1	aggregates too large
17	P2-BT-100-2	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	2	aggregates too large
18	P2-BT-100-3	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	3	aggregates too large
19	P2-BT-100-4	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	4	aggregates too large
20	P2-BT-100-5	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	5	*aggregates too large*
21	S7-BT-200-1	SIGMA C'IN C-3387	40mL B+5mL TH	'-200	1	ice test (I2) 3% ice
22	S7-BT-200-2	SIGMA C'IN C-3387	40mL B+5mL TH	'-200	2	ice test (I2) 5% ice
23	S7-BT-200-3	SIGMA C'IN C-3387	40mL B+5mL TH	'-200	3	ice test (I2) 10% ice
24	S7-BT-200-4	SIGMA C'IN C-3387	40mL B+5mL TH	'-200	4	ice test (I2) 0% ice
25	S7-BT-200-5	SIGMA C'IN C-3387	40mL B+5mL TH	'-200	5	ice test (I2) 5% ice
26	P2-BT-200-1	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-200	1	ice test (I1) 40% ice
27	P2-BT-200-2	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-200	2	ice test (I1) 15% ice
28	P2-BT-200-3	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-200	3	ice test (I1) 30% ice
29	P2-BT-200-4	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-200	4	ice test (I1) 30% ice
30	P2-BT-200-5	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-200	5	ice test (I1) 40% ice
31	S2-BT-200-1	SIGMA C'SAN C-0792	40mL B+5mL TH	'-200	1	
32	S2-BT-200-2	SIGMA C'SAN C-0792	40mL B+5mL TH	'-200	2	
33	S2-BT-200-2.86	SIGMA C'SAN C-0792	40mL B+5mL TH	'-200	2.86	

	A	B	C	D	E	F
34	S6-BT-200-1	SIGMA C'IN C-4666	40mL B+5mL TH	'-200	1	
35	S2-BT-100-3	SIGMA C'SAN C-0792	40mL B+5mL TH	'-100+200	3	
36	S2-BT-100-4	SIGMA C'SAN C-0792	40mL B+5mL TH	'-100+200	4	
37	S2-BT-100-5	SIGMA C'SAN C-0792	40mL B+5mL TH	'-100+200	5	ice test (I3) 15% ice
38	S6-BT-100-2	SIGMA C'IN C-4666	40mL B+5mL TH	'-100+200	2	
39	S6-BT-100-3	SIGMA C'IN C-4666	40mL B+5mL TH	'-100+200	3	
40	S7-BT-100-10	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	10	ice test (I4) 60% ice
41	S7-BT-100-15	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	15	ice test (I4) 80% ice
42	P2-BT-100-10	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	10	ice test (I4) 80% ice
43	P2-BT-100-15	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	15	ice test (I4) 60% ice
44	P2-BT-100-D	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-100+200	dip	ice test (I3) 0% ice
45	P2-BT-200-D	PFALTZ & BAUER C'IN	40mL B+5mL TH	'-200	dip	ice test (I3) 80% ice
46	S7-BT-100-D	SIGMA C'IN C-3387	40mL B+5mL TH	'-100+200	dip	ice test (I3) 80% ice
47	S7-BT-200-D	SIGMA C'IN C-3387	40mL B+5mL TH	'-200	dip	ice test (I3) 0% ice
48	S7-GT-100-3	SIGMA C'IN C-3387	40mL G+5mL TH	'-100+200	3	ice test (I5) 10% ice
49	S7-GT-100-4	SIGMA C'IN C-3387	40mL G+5mL TH	'-100+200	4	ice test (I5) 10% ice
50	S7-GT-100-5	SIGMA C'IN C-3387	40mL G+5mL TH	'-100+200	5	ice test (I5) 10% ice
51	S7-GT-100-10	SIGMA C'IN C-3387	40mL G+5mL TH	'-100+200	10	ice test (I5) 20% ice
52	P2-G+20-1	PFALTZ & BAUER C'IN	40mL G+5mL TH	'+20	1	dsp. % is total paint wt.
53	P2-G+20-2	PFALTZ & BAUER C'IN	40mL G+5mL TH	'+20	2	dsp. % is total paint wt.
54	P2-G+20-3	PFALTZ & BAUER C'IN	40mL G+5mL TH	'+20	3	dsp. % is total paint wt.
55	P2-G-20-1	PFALTZ & BAUER C'IN	40mL G+5mL TH	'+20	1	aggregates way too large
56	P2-G-20-2	PFALTZ & BAUER C'IN	40mL G+5mL TH	'+20	2	ice test (I5) 20% ice
57	P2-G-20-3	PFALTZ & BAUER C'IN	40mL G+5mL TH	'+20	3	ice test (I5) 30% ice
58	P2-GT-80-3	PFALTZ & BAUER C'IN	40mL G+5mL TH	'-80+100	3	ice test i(6) 20% ice
59	P2-GT-80-4	PFALTZ & BAUER C'IN	40mL G+5mL TH	'-80+100	4	ice test i(6) 20% ice
60	P2-GT-80-5	PFALTZ & BAUER C'IN	40mL G+5mL TH	'-80+100	5	ice test i(6) 10% ice
61	P2-GT-80-10	PFALTZ & BAUER C'IN	40mL G+5mL TH	'-80+100	10	ice test i(6) 10% ice
62	CONTROL-G	NONE	40mL Gray only	***	***	glossy finish
63	CONTROL-GT	NONE	40mL G+5mL TH	***	***	glossy finish
64	S7-GT-80-3	SIGMA C'IN C-3387	40mL G+5mL TH	'-80+100	3	ice test i(6) 10% ice
65	S7-GT-80-5	SIGMA C'IN C-3387	40mL G+5mL TH	'-80+100	5	ice test i(6) 10% ice
66	S7-GT-80-10	SIGMA C'IN C-3387	40mL G+5mL TH	'-80+100	10	ice test i(6) 10% ice

	A	B	C	D	E	F
67	SI-GT-?-3	SIGMA CHITIN C-3641	40mL G+5mL TH	not sieved	3	ice test i(7) 10% ice
68	SI-GT-?-5	SIGMA CHITIN C-3641	40mL G+5mL TH	not sieved	5	ice test i(7) 5% ice
69	SI-GT-?-10	SIGMA CHITIN C-3641	40mL G+5mL TH	not sieved	10	ice test i(7) 5% ice
70	SI-GT-?-15	SIGMA CHITIN C-3641	40mL G+5mL TH	not sieved	15	ice test i(7) 5% ice
71	SI-GT-200-3*	SIGMA CHITIN C-3641	40mL G+5mL TH	'-200	3	ice test i(7) 20% ice
72	SI-GT-200-3	SIGMA CHITIN C-3641	40mL G+5mL TH	'-200	3	ice test i(7) 10% ice
73	SI-GT-200-5	SIGMA CHITIN C-3641	40mL G+5mL TH	'-200	5	ice test i(7) 10% ice
74	SI-GT-200-10	SIGMA CHITIN C-3641	40mL G+5mL TH	'-200	10	ice test i(7) 5% ice
75	SI-GT-140-3	SIGMA CHITIN C-3641	40mL G+5mL TH	'-140+200	3	ice test i(8) 10% ice
76	SI-GT-140-5	SIGMA CHITIN C-3641	40mL G+5mL TH	'-140+200	5	ice test i(8) 10% ice
77	SI-GT-140-10	SIGMA CHITIN C-3641	40mL G+5mL TH	'-140+200	10	ice test i(8) 10% ice
78	S7-GT-100-3	SIGMA C'IN C-3387	20mL G+2.5mL TH	'-100+200	3	ice test i(9) 20% ice
79	S7-GT-100-4	SIGMA C'IN C-3387	20mL G+2.5mL TH	'-100+200	4	ice test i(9) 30% ice
80	S7-GT-100-5	SIGMA C'IN C-3387	20mL G+2.5mL TH	'-100+200	5	ice test i(9) 30% ice
81	S7-GT-100-10	SIGMA C'IN C-3387	20mL G+2.5mL TH	'-100+200	10	ice test i(9) 20% ice
82	S7-GT-100-15	SIGMA C'IN C-3387	20mL G+2.5mL TH	'-100+200	15	ice test i(9) 15% ice
83	S7-GT-100-20	SIGMA C'IN C-3387	20mL G+2.5mL TH	'-100+200	20	ice test i(9) 10% ice
84	PS-GT-45-3	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-45+80	3	ice test i(10) 20% ice
85	PS-GT-45-5	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-45+80	5	ice test i(10) 20% ice
86	PS-GT-45-10	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-45+80	10	ice test i(10) 20% ice
87	CB-GT-45-3	CTC ORGANICS C'SAN	20mL G+2.5mL TH	'-45+80	3	ice test i(10) 20% ice
88	CB-GT-45-5	CTC ORGANICS C'SAN	20mL G+2.5mL TH	'-45+80	5	ice test i(10) 20% ice
89	CB-GT-45-10	CTC ORGANICS C'SAN	20mL G+2.5mL TH	'-45+80	10	ice test i(10) 30% ice
90	PS-GT-80-3	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-80+100	3	ice test i(11) 20% ice
91	PS-GT-80-5	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-80+100	5	ice test i(11) 20% ice
92	PS-GT-80-10	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-80+100	10	ice test i(11) 25% ice
93	CA-GT-100-3	CTC ORGANICS C'IN	20mL G+2.5mL TH	'-100+200	3	
94	CA-GT-100-5	CTC ORGANICS C'IN	20mL G+2.5mL TH	'-100+200	5	
95	CA-GT-100-10	CTC ORGANICS C'IN	20mL G+2.5mL TH	'-100+200	10	
96	CB-GT-100-3	CTC ORGANICS C'SAN	20mL G+2.5mL TH	'-100+200	3	ice test i(12) 15% ice
97	CB-GT-100-5	CTC ORGANICS C'SAN	20mL G+2.5mL TH	'-100+200	5	ice test i(12) 15% ice
98	CB-GT-100-10	CTC ORGANICS C'SAN	20mL G+2.5mL TH	'-100+200	10	ice test i(12) 15% ice
99	PS-GT-100-3	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-100+200	3	
100	PS-GT-100-5	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-100+200	5	
101	PS-GT-100-10	PROTAN SEA CURE C'IN	20mL G+2.5mL TH	'-100+200	10	

Polished and Dipped Samples

Sample S2-BT-100-5 was polished on the Buehler Ecomet 111 polisher/grinder using 1 micron Al203 grinding powder in water for about five minutes to determine if full exposure of the chitin would increase the icephobic characteristics. Samples P2-BT-100 & 200-D and S7-BT-100 & 200-D were painted with the standard mixture (40ml paint + 5ml thinner), then immediately dipped in the corresponding chitin type & size. This produced a sample with exposed chitins on the surface and black paint underneath.

Both the polished and the dipped samples above were later subjected to the icebox freeze tests and showed no significant increases in icephobic qualities. The results will be shown later in Icephobic Test (I3).

Ice Box Icephobic Tests

The comments section in Table "ICE.XLS" refers to "ice test" data produced using the methods explained in ONRC1, pg. 8, 4-30-90. The following observations were made during each of the Icephobic tests below:

I1 - Initial icephobic tests showed the chitin coating to be substantially better than standard paint in anti-icing properties, however, ice repulsion is not 100% at this time.

I2 - Although lower ice percentages were seen with this test then with I1, the control sample (CONTROL-BT) also had less ice adhering to its surface. Apparently a higher percentage of chitin/chitosan is needed for improved icephobic qualities.

I3 - One micron polishing did not improve the icephobic qualities of sample S2-BT-100-5 substantially. It is difficult to explain (on the dipped samples) why different types and sizes of chitins showed either no ice (0%) forming or a great deal (80%) showing.

I4 - A higher percentage of ice formed on the samples than the control. It may be due to the larger surface area created by the chitins on the painted region. This would cause the samples to initially hold more water.

I5 - Same as I4 above.

I6 - This test showed all of the chitin treated samples to be more icephobic than the control (non-treated) standard. The -80 mesh covers the surface evenly, but appears to be too large for our application.

I7 - The purified chitin showed very good icephobic qualities. The test showed that the higher dispersal percentage chitins repelled ice better than the lower concentration samples. The unsieved samples were slightly more icephobic than the sieved -200 mesh samples, although visually not as congruous on the dried test strips.

I8 - The -140 mesh samples were not as icephobic as the unsieved samples in test I7.

I9 - The icephobic qualities improved with the increasing dispersal concentrations. A 20% dispersal appears to be the saturation point of chitin allowed in the mixture.

I10 - With the relatively large particle size used (-45+80 mesh) the samples tend to hold water between the grains. This explains why there isn't a decrease in ice percentages with the higher dispersal percentages.

I11 - The -80 +100 mesh tends to hold more water as in test I10 above.

I12 - The -100 +200 mesh showed better icephobic qualities then the coarser meshes used in tests I10 and I11.

Ice Box Freeze Test Summary

The icephobic tests using the ice box for a cooling medium showed some definite trends. First, the finer particle size samples with a 10 to 15% dispersal exhibited the best anti-icing properties. Second, the coarser meshes held water between the grains causing higher ice percentage readings. Third, 20% was the saturation point of chitins in the paint mixture. Fourth, dipping the painted surface into chitins did not provide a feasible surface layer. Fifth, sieving into specific mesh sizes helped provide a uniform coating and sixth, purified chitin was slightly more icephobic then standard brands. Another system will now be developed to try and more closely simulate marine conditions.

Marine Bath Icephobic Tests

A salt water bath freeze system was developed to test the icephobic qualities of the chitin/chitosan painted samples in a marine environment. The fabricated system used two 1/4" stainless steel coils 12cm high by 7cm, connected with rubber surgical tubing. The coils were then attached to the inlet/outlet coils of a Fisher Scientific "Isotemp Refrigerated Circulator" Model 9500 filled with 8 liters of 50% methanol, 50% D.I. H_2O. The coils were then placed in a cylindrical vessel 22cm deep by 25cm diameter.

ICE.XLS

				ICE	TESTS	I1 - I12						
DISPERSAL %	I1	I2	I3	I4	I5	I6	I7	I8	I9	I10	I11	I12
0	75	10	20	40	10	40	40	20	20	30	50	20
1	40	3	dipped	***	***	***	***	***	***	***	***	***
2	15	5	samples	***	20	***	***	***	***	***	***	***
3	30	10	(all same	***	20	20	10	10	20	20	20	15
4	30	0	disp. %)	***	10	20	***	***	30	***	***	***
5	40	5	0	***	10	10	5	10	30	20	20	15
10	***	***	0	60	20	10	5	10	20	20	25	15
15	***	***	80	80	***	***	5	***	15	***	***	***
20	***	***	80	***	***	***	***	***	10	***	***	***
	Note:	" *** "	indicates	no	sample	tested						

This vessel was surrounded by foam padding insulation then placed in a styrofoam box. Sea water was simulated by adding 38g/1 (8 liters total) of "Instant Ocean" aquarium salt (Aquarium Systems, 8141 Tyler Blvd., Mentor, OH 44060). This concentration had a specific gravity of 1.022 g/cm3 @ 22oC.

To test the samples' icephobic characteristics, two samples, PS-GT-100-5 and PS-GT-100-10 plus one control sample, were hung from the cooling coils in the marine bath. The temperature was set to -15oC on the refrigerated circulator. A Marineland Penguin Power Head Model PH550 "circulator/aerator" pump was placed on the side of the vessel submerged. An Omega digital thermometer thermocouple was placed in the bath next to the coils for temperature readings. The coils began freezing at -4.5oC with the circulator/aerator pump on and at -1.5oC with the pump off. It was unclear by observation when the samples began freezing.

Test strips 36cm X 8mm were painted on both sides for the next test. These samples were marked with a GT"L" to designate the extra long length. Samples PS-GTL-100-10 and CONTROL-GTL were wrapped once around the outlet cooling coil of the refrigerated circulator. Sample PS-GTL-100-5 was wrapped once around the inlet coil. The aerator pump was turned off and the refrigerated circulator was set to -15oC. This dropped the temperature of the marine bath at a rate of approx. 1.7oC per minute. Ice began forming on the outlet coil at -1.5oC. PS-GTL-100-10 and CONTROL-GTL repelled ice until -2.7oC. Ice began forming around the inlet coil at -2.0oC. PS-GTL-100-5 repelled ice until -2.4oC. Crystallization was slower on the inlet coil because of the warming effects of the bath. A specific gravity reading taken at -3.0oC was 1.021 g/cm3.

Subsequent tests made with the aeration pump off permitted the bath to reach lower temperatures before freezing started (-4.5oC). The system crystallized in two different ways. With the aerator on the system freezes throughout the entire bath with some ice floating to the top and covering the surface. The aerator off induced the system to freeze around the coils only with the outlet coil freezing before the inlet coil.

After these initial tests were completed an experiment was designed to compare the freezing temp. of the bath with salinity and specific gravity with salinity. "Instant Ocean" sea salt was added to 8 liters of tap water in 10 g/1 increments. After dissolving the salt, the specific gravity was recorded at 15.5oC. The refrigerated circulator was set for -20oC. When the solution crystallized around the coils the initial "freezing point" and a stabilized "after freezing" readings were taken. The results are shown in Figure 1. Notice that the freezing point temperature has still not stabilized. The test will be continued until a maximum freezing point at equilibrium can be established.

Figure 2 illustrates the specific gravity data taken at 15.5oC for each 10 g/l salt increment. As expected the relationship is linear throughout except for a small deviation at the highest salt concentrations. This is probably due to evaporation. This data will also be recorded until a f.p. equilibrium is reached.

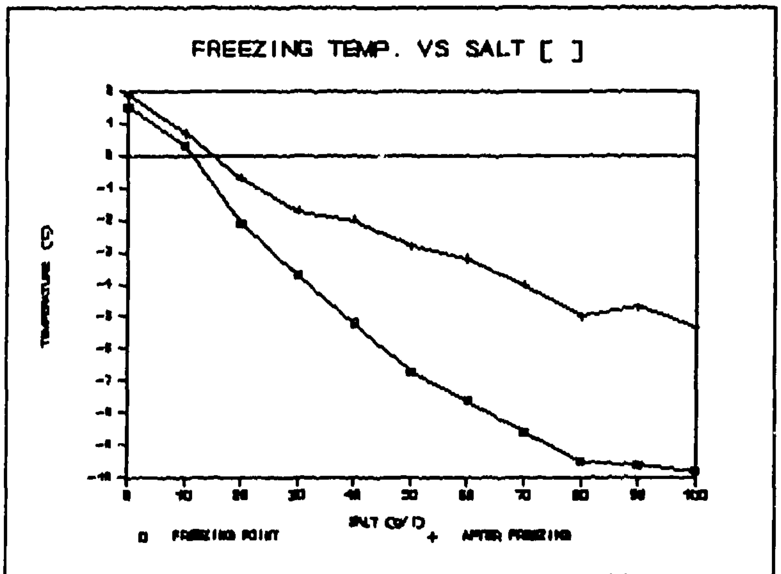

Figure 1

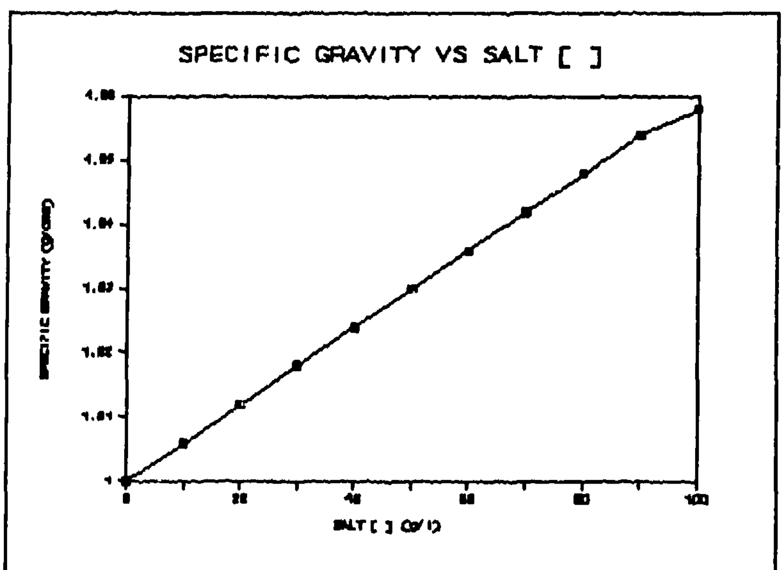

Figure 2

Fungi Tests

Twenty-three pairs of painted test strips with chitin/chitosan additives plus eight control samples were selected for the initial fungi testing. Aspergillus oryzae (ATCC No. 10196) and Aspergillus niger (ATCC No. 9642) were chosen for the fungi representatives. The YM agar medium was prepared as follows:

Bacto YM Agar	
Bacto Yeast Extract	3 gm/l
Difco Malt Extract	3 gm/l
Bacto Peptone	5 gm/l
Bacto Dextrose	10 gm/l
Bacto Agar	20 gm/l

Final pH 6.2 at 25^{o}C

To rehydrate, the appropriate amount was suspended in 1 liter 0.2 μm Nanopure H_2O. The agar was heated to boiling to dissolve completely. The solution was then placed in the autoclave for 20 minutes at 15 pounds pressure. The solution was poured in petri dishes, then cooled and stored at <30^{o}C.

After allowing the cultures to grow for ten days, one each of the 23 pairs were placed three to a petri dish in the two different cultures and stored in a light free environment at ambient temperature. Figure "Fungi1.XLS", below, shows the order of placement. When observations begin the samples will be compared on the basis of 1.) Chitin/chitosan type 2.) Paint type 3.) Mesh size and 4.) Dispersal percentage.

RESULTS AND CONCLUSIONS

Dispersal percentages in the 10-15% range are the optimum for icephobic qualities. Mesh sizes of -200 and smaller are the optimum for our applications. SEM inspection was not as effective as the stereo microscope for evaluation of regional areas of the samples. Polished or dipped samples produced undesirable results icephobically. The icebox anti-icing evaluations provided a framework for comparison with the more sophisticated oceanic marine bath system. Refinement of the marine bath system is underway for more qualitative information on icephobic traits. The Protan Sea Cure 350 purified chitin looks best in both preblend mixing and in the icephobic testing. Preliminary information will soon be analyzed on the fungi testing. Analytical methods are being studied to attempt stable chemical alterations of the chitin before mixing with the paint. Also, operations have begun on ASTM testing and evaluation of the materials already produced. According to recent information, new products have been introduced in a variety of forms (powder, solution, gel, films, fiber, bead and derivatized). These will be investigated.

FUNGI1.XLS

	1	2	3	4	5
Aspergillus oryzae 10196	CONTROL-BT	CONTROL-GT	PS-GT-100-5	CA-GT-100-10	CONTROL-BT
	S2-BT-100-3	PS-GT-45-5	CB-GT-100-5	P2-BT-100-1	P2-BT-100-4
	S2-BT-100-5	PS-GT-80-5	CA-GT-100-5	P2-BT-100-2	P2-BT-100-5
Aspergillus niger 9642	CONTROL-BT	CONTROL-GT	PS-GT-100-5	CA-GT-100-10	CONTROL-BT
	S2-BT-100-3	PS-GT-45-5	CB-GT-100-5	P2-BT-100-1	P2-BT-100-4
	S2-BT-100-5	PS-GT-80-5	CA-GT-100-5	P2-BT-100-2	P2-BT-100-5

	6	7	8	9
Aspergillus oryzae 10196	P2-BT-100-10	P2-BT-200-5	S7-GT-100-15	CONTROL-GT
	P2-BT-100-15	S7-GT-100-5	S7-BT-100-15	S7-GT-100-20
	S6-BT-100-3	S7-BT-100-5	S7-BT-200-5	P2-BT-100-3
Aspergillus niger 9642	P2-BT-100-10	P2-BT-200-5	S7-GT-100-15	CONTROL-GT
	P2-BT-100-15	S7-GT-100-5	S7-BT-100-15	S7-GT-100-20
	S6-BT-100-3	S7-BT-100-5	S7-BT-200-5	P2-BT-100-3

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